This chapter describes a novel method of dispersion of thiol-protected gold nanoparticles in two different lyotropic liquid crystalline phases viz, the columnar hexagonal phase (H1 phase) of Triton X-100/water system and the reverse columnar hexagonal phase (H2 phase) of AOT system. We find that the dispersion of the nanoparticles retains the mesophase structure with an increase in the liquid crystalline order in both the H1 and H2 phases. These types of dispersions of the nanoparticles in the liquid crystalline matrix are interesting as they possess an ordered structure of the liquid crystalline phase while retaining the unique properties of the nanomaterials. This chapter also discusses the results of the ionic conductivity studies of the H1 phase formed by Triton X-100/water system. Surprisingly the ionic conductivity values of these systems are very high even though the phase is formed by the nonionic surfactant, Triton X-100. We find that the addition of gold nanoparticles increases the liquid crystalline order and also the ionic conductivity of the medium. On the other hand, the addition of chaotropic agents like urea results in a decrease in the ionic conductivity values. Based on these observations, the very high ionic conductivity of these systems could be explained on the basis of Grotthus mechanism, which rely on the proton transfer pathways by the water clusters. Hence the conductivity of these systems resembles the proton
conductivity in proteins as the same mechanism takes place in both the systems.

3.1 Introduction

The lyotropic liquid crystalline phases possess potential applications in both fundamental research and in the technology [1]. These lyotropic phases are also important due to their resemblance to biological systems as many of the proteins have been shown to form such ordered phases in the aqueous medium. For example, the lipids are known to form lamellar phase by forming the bilayer structure in the biological environment as well as in aqueous solutions. The lyotropic liquid crystalline phases formed by nonionic surfactants are of special interest as they do not contain any ionic species in the phase. Due to this, the interference of ions including the counter ions of the surfactants can be avoided. The nonionic surfactant Triton X-100 in the aqueous medium has been shown to form a hexagonal columnar phase and a lamellar phase [2]. A detailed investigation of the columnar phase (H1 phase) of the system was studied by Ahir et al. using a variety of experimental techniques [3]. Galatanu et al. have studied the phase diagram of the ternary system containing polyacrylic acid (PAA), Triton X-100 and water. They have shown that the PAA changes the melting point of the liquid crystalline phases of the Triton X-100/water system without changing the columnar hexagonal order where the polyacrylic acid interacts with the polyethoxy chain of Triton X-100 molecules [4].

The columnar hexagonal phase (H1 phase) of this system has been used as a medium for different applications. Nickel deposits formed in this medium with the addition of nickel salts were found to be highly porous and explored for the supercapacitor applications [5]. This H1 phase has also been explored for the formation of self-assembled monolayers of organic thiols on the gold surface and the results have shown that such monolayers are more compact compared to the monolayers formed through typical solutions [6]. The dispersion of carbon nanotube in the H1 phase has been reported by Regev et al. where they have shown that single walled carbon nanotubes can be well dispersed in the medium without altering the liquid crystalline order [7]. In the present chapter, we describe our experimental results on the dispersion of thiol-protected gold nanoparticles in the H1 phase. The chapter also describes the ionic conductivity studies in this medium. The effect of addition of gold
nanoparticles and urea on the ionic conductivity is also described in this chapter.

3.2 Dispersion of GNP\(s\) in the liquid crystalline phase

Integration of nanoparticles with liquid crystals is of interest for the past several years. Lee et al. have reported the synthesis of silver nanoparticles in the H1 phase of Triton X-100/water system [8]. In their studies, the Triton X-100 acts as a reducing agent while the columnar phase has controlled the growth and aggregation of the silver nanoparticles. They have shown that the growth of these nanoparticles has not altered the columnar structure of the Triton X-100/water system. Triton X-100 molecules are also shown to be capable of reducing palladium ions to Pd nanoparticles [9]. Wang et al. have reported the synthesis of nano and micro plates of gold with triangular or hexagonal shape by the reduction of chloroauric acid in the liquid crystalline phase formed by polyethoxy-polypropyloxy-polyethoxy block copolymers where the oxyethylene groups act as the reducing agents for Au(III) ions [10]. Gascon et al. have reported the synthesis of narrow-dispersed gold nanoparticles in the smectic phase than in the isotropic phase [11]. The preparation of gold fractal structures in the lamellar phase has also been reported in the literature [12]. It was shown that the gold nanoparticles form inside the multilamellar vesicles and the relationship between the lamellar arrangement and the nanoparticle size has been studied [13]. The synthesis of micron size gold nanoplates and nanobelts in a lyotropic liquid crystalline phase made up of block copolymers has also been demonstrated previously [14].

Dispersion of nanomaterials in liquid crystalline systems provides several advantages due to the unique properties of these nanomaterials and the self-organised structure of the liquid crystalline phases. There are several reports on the synthesis of nanoparticles in the presence of surfactants and micelles. Herrera et al. have prepared the nanoparticles using surfactants in a reverse micelle [15], while Jana et al. have studied the gold nanoparticles that are covered with CTAB molecules [16]. Ghosh et al. have reported Triton X-100 as stabiliser for gold nanoparticles [17]. The synthesis and stabilisation of nanoparticles by AOT and its incorporation into the reverse micelles of AOT have also been reported [18; 19].

The gold nanoparticles in an aqueous micellar medium provide potential applications for both drug delivery as well as immunoassay studies. Here, we describe our studies on the in-
tegration of hexanethiol and cyanobiphenylthiol (10CB-thiol)-protected gold nanoparticles in highly ordered lyotropic hexagonal columnar liquid crystalline systems. The hexagonal columnar phase was made either by a Triton X-100/water system or by a pure AOT system. While Triton X-100/water system has a normal hexagonal columnar structure (H1 phase), AOT exhibits a reverse hexagonal columnar liquid crystalline phase (H2 phase) [20; 21; 22; 23; 24]. The dispersions were characterised using polarising optical microscopy (POM) and small-angle X-ray scattering (SAXS) studies.

3.2.1 Experimental Procedures

**Chemicals:** Triton X-100 (Spectrochem), HAuCl₄·3H₂O (Aldrich), NaBH₄ (Aldrich), hexanethiol (Aldrich), tetracaylammonium bromide (Aldrich), AOT (sodium (2-ethylhexyl)sulfosuccinate) (SD fine Chem. Ltd), and toluene (Aldrich) were used as received. 10CB Thiol (4′-[10-sulfanyldecyl]oxy][1,1′-biphenyl]-4-carbonitrile) was synthesised by S. Kumar et al. as reported earlier [25]. Millipore water of resistivity 18 MΩ·cm was used for the preparation of all the samples.

**Gold nanoparticle Preparation:** Gold nanoparticles (GNPs) covered with hexanethiolate monolayer were synthesised by S. Kumar et al. [26; 27] by following the literature method [28; 29]. In brief, a solution of tetracaylammonium bromide (1.1 g) in toluene (65 mL) was added with stirring to a solution of 158 mg of HAuCl₄·3H₂O. This solution was stirred for 20 min and mixed with n-hexanethiol (142 mg) with further stirring for 10 min. A solution of 450 mg of NaBH₄ dissolved in 5 mL of water was added to the above mixture. The reaction mixture was stirred at room temperature for 24 h. The organic phase was separated, evaporated to about 2-3 mL in a rotary evaporator under vacuum at room temperature, mixed with 50 mL of ethanol and centrifuged at 5000 rpm for 1 h. The supernatant liquid was removed and the resulting hexanethiol-protected gold nanoparticles were dissolved in about 1 mL of dichloromethane and precipitated with ethanol. The centrifugation and re-dispersal process was repeated several times to ensure the complete removal of noncovalently bound organic material. Removal of the solvent afforded 60 mg of hexanethiol-capped gold nanoparticles (C₆GNP). It has been shown that this procedure results in the formation of GNPs with an average composition of Au₁₄₀[S(CH₂)₅-CH₃]₃₃ [29]. The 10CB-thiol stabilised gold nanopar-
articles (10CB-GNP) were prepared by following a similar procedure.

**Preparation of GNP Dispersions:** The lyotropic hexagonal columnar liquid crystalline phase (H1 phase) was prepared with a composition of 42 wt% Triton X-100 and 58 wt% water as described in chapter 2, by following the procedure reported earlier [6; 30]. A total of 2 mL of this mixture was heated to about 35 °C to the isotropic phase, and 12 mg of the hexanethiol functionalised GNPs were dispersed in this medium. This was followed by ultrasonication for 10 min and was allowed to cool down to 25 °C. Two more samples with compositions of 2.4 mg of GNP/2 mL of H1 phase and 1 mg of GNP/2 mL of H1 phase were prepared following the same process. For 10CB-thiolated GNP, two samples of compositions of 1 mg of GNP/2 mL of H1 phase and 0.5 mg of GNP/2 mL of H1 phase were prepared by the same procedure. The samples were homogeneous in nature, indicating that the GNPs are well-dispersed in the H1 phase and found to be stable for several days. For the preparation of GNP dispersions in AOT, 1 mg of the nanoparticles was mixed with 2 g of pure AOT, that was dissolved in diethyl ether. This solution was mixed well, and the solvent was evaporated to obtain the GNP dispersion in AOT. A picture of these dispersion are shown in Figure 3.1.

**Characterisation:** Scanning tunneling microscopic images were taken using an STM that has been fabricated in our laboratory. The nanoparticles were dispersed over an ITO coated glass plate. The scanning was carried out under constant current mode with a bias voltage of +100 mV and a reference current of 1 nA. Electrochemically etched tungsten wire was used as the tip for scanning. The images were analysed using Scanning Probe Image Processor software (SPIP, Image Metrology, Denmark). The polarising optical microscopic studies of the samples were carried out using an Olympus POM instrument. The textures were taken by sandwiching the samples between glass slides and cover slips. In the Triton X-100/water system, the samples were heated to the isotropic temperature and the images were obtained while cooling. For the AOT samples, the textures were taken at room temperature. The small-angle X-ray scattering studies were carried out using an X-ray diffractometer (Rigaku, UltraX 18) operating at 50 kV and 80 mA using Cu Kα radiation having a wavelength of 1.54 Å. Samples were prepared by filling the capillary with the liquid crystal or the GNP dispersion and sealed. All the scattering studies were carried out at room temperature.
3.2.2 Results and Discussion

3.2.2.1 Dispersion of GNPs in Triton X-100/Water System

From the STM studies, as shown in Figure 3.2, the size of hexanethiol capped gold nanoparticles was measured to be about 3.6 nm. This measured size includes the nanoparticle core and the hexanethiol molecules around the core that are used to stabilise the nanoparticles.

Figure 3.2: a) Scanning tunneling microscopic image of the hexanethiol capped gold nanoparticle and b) line profile for the image

Figure 3.3(a) shows the texture of pure H1 phase formed by the Triton X-100/water system and b) H2 phase of AOT.
system. Figure 3.3(b) and 3.3(c) show the textures obtained for the dispersions containing 1 mg of GNP/2 mL of Triton X-100/water system for the hexanethiolated and 10CB-thiolated GNPs, respectively. All these dispersions show the typical texture of H1 phase, which were stable down to room temperature. These images indicate that the H1 phase is retained in all these samples. We have observed that the temperature corresponding to the isotropic to columnar phase transition varies with the GNP concentration in these dispersions. The transition temperature of pure H1 system is 29 °C, while for the sample containing 1 mg of C6-GNP/2 mL of H1 phase, the transition temperature has shifted to 33.1 °C. This increase in the transition temperature clearly shows that the nanoparticles stabilise the H1 phase of the Triton X-100/water system. But at higher concentrations of GNPs, the transition temperature again decreases (32.9 °C for 2.4 mg of GNP/2 mL of H1 phase and 31.9 °C for 12 mg of GNP/2 mL of H1 phase), which may be attributed to the beginning of the phase separation. For the 10CB-thiolated GNPs, the transition temperature is 33.1 °C for the concentration of 0.5 mg of GNP/2 mL of H1 phase and 33.6 °C at the concentration of 1 mg of GNP/2 mL of H1 phase.

Figure 3.3: Polarising optical micrographic textures obtained for a) pure H1 phase of Triton X-100/water system, b) C6-GNP/H1 phase and c) 10CB-GNP/H1 phase. Scale bar=100 μm

For a better understanding of the liquid crystalline phase of the dispersions, we have carried out the small angle X-ray scattering (SAXS) studies of the pure and the GNP dispersed Triton X-100/water systems. Figure 3.4 shows the intensity vs. scattering vector q for the different samples. It is observed that the peaks in Figure 3.4 follow the ratio 1:√3:√4:√7. This indicates that the columnar hexagonal order with P6mm space group exists in the pure Triton X-100/water system as well as in the dispersions [31]. This is in agreement with the
POM results described above. From the scattering vector, we have calculated the $d$ spacing for all the samples and are presented in Table 3.1, where the different peaks corresponds to (1,0), (1,1), (2,0), and (2,1) scattering planes in the phase. We have calculated the lattice parameters from the peak corresponding to the (1,0) plane using the equation [32]

$$a = \frac{2d}{\sqrt{3}}$$

The main scattering peak in the SAXS corresponds to a lattice parameter value of 60.66 Å, 60.01 Å and 61.60 Å for the pure H1 phase, C6-GNP-dispersed H1 phase, and 10CB-GNP-dispersed H1 phase, respectively.

![Scattering vector vs. intensity plots obtained from the SAXS for a) pure H1 phase of Triton X-100/water system, b) C6GNP/H1 phase and c) 10CB-GNP/H1 phase](image)

Table 3.1: The $d$ values in Å of the Triton X-100/Water system and 1 mg of GNP/2 mL of Triton X-100/Water system measured by SAXS studies at room temperature

<table>
<thead>
<tr>
<th></th>
<th>$d_1$</th>
<th>$d_2$</th>
<th>$d_3$</th>
<th>$d_4$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure H1 phase</td>
<td>52.54</td>
<td>30.42</td>
<td>26.29</td>
<td>-</td>
</tr>
<tr>
<td>C6-GNP/H1 phase</td>
<td>51.97</td>
<td>29.85</td>
<td>26.15</td>
<td>20.80</td>
</tr>
<tr>
<td>10CB-GNP/H1 phase</td>
<td>53.35</td>
<td>31.04</td>
<td>27.20</td>
<td>21.88</td>
</tr>
</tbody>
</table>

Since the change in the $d$ values is small for the GNP-dispersed system compared to the pure H1 phase, it indicates that the dispersions do not significantly alter the columnar arrangement of the Triton X-100/water system in both the dispersions. Due to the large size
of the nanoparticles of about 3.6 nm, they can not be accommodated within the core of the micelles, but are present outside the boundaries of the columns and interdomain spacings. This observation is in agreement with the SAXS studies. If the gold nanoparticles have to reside inside the hydrophobic core of Triton X-100/water micelles, then the large size of the thiol stabilised GNPs would have severely distorted the hexagonal columns (about 5 nm). Such a distortion should have resulted in a large increase in the \( d \) spacing as measured by the SAXS studies. On the other hand, the GNPs will prefer the inter-domain spaces due to higher entropic gain instead of being confined inside the hydrophobic columns. The nanoparticles have sufficient space between the domain planes.

It is clear from the Figure 3.4 and the Table 3.1 that all the GNP-dispersed systems show the columnar hexagonal phase. The additional Bragg peak at the \( \sqrt{7} \) position due to the (2,1) reflections shows that the H1 phase is more ordered within the core after the addition of GNPs. For the hexanethiol-GNP dispersed systems, the \( d \) values have decreased compared to the pure H1 phase. This can be explained on the basis of our proposed model of the dispersions. For the hexanethiol capped GNPs, the terminal groups are hydrophobic in nature, while for the micelles, the outer boundary is hydrophilic. As a result, for minimising the hydrophobic-hydrophilic interactions between the GNPs and the polar boundaries of the cylindrical micelles, the individual columns will tend to shrink, which results in the reduction of \( d \) values. On the other hand, we have observed a small increase in the \( d \) spacing for the 10CB-thiolated GNP dispersion. Here the interaction between the terminal polar cyano group of the nanoparticles and the water molecules on the micelle leads to a small expansion of the micellar core that leads to an increase in the \( d \) values.

Assuming a spherical shape, and the average size of these nanoparticles to be 4 nm with the molecular formula for the hexanethiol stabilised GNPs to be \( \text{Au}_{140}\{\text{S(CH}_2)_2\text{CH}_3\}\text{S}_3 \) [28; 29], we have calculated the molar ratio and the volume fraction of these dispersions. We obtain a volume fraction of about 1:3300 for the GNP:H1 phase for the dispersion of 1 mg C6-GNP/H1 phase. This indicates that the number of GNPs in the dispersions is not significantly high to perturb the \( d \) spacing of the columns, which is in agreement with our POM and small-angle X-ray scattering studies.
3.2.2.2 Dispersion of GNPs in AOT

The dispersions of both hexanethiolated and 10CB-thiolated GNPs in the reverse hexagonal phase of AOT (H2 phase) have been prepared as described before in the experimental section. A picture of the dispersion is shown in Figure 3.1(b). Since the nanoparticles may not be stable up to the transition temperature of AOT (of about 180 °C), the polarising optical micrographic images were taken at room temperature without heating and subsequent cooling as is done in the case of H1 phase of Triton X-100/water system discussed earlier. Figure 3.5 presents the POM images obtained for the pure AOT and the dispersions. It is clear from the figure that the pure AOT forms a reverse hexagonal phase (H2 phase) and the dispersions have retained the H2 phase.

![Figure 3.5: Polarising optical micrographic textures obtained for a) pure H1 phase of AOT, b) C6-GNP/AOT and c) 10CB-GNP/AOT. Scale bar=50 μm](image)

We have carried out SAXS studies of the pure AOT as well as the GNP-dispersed AOT systems at room temperature. Figure 3.6 represents the diffraction patterns obtained for these samples, where the intensity is plotted against the scattering vector q. In the case of C6-GNP and 10CB-GNP-dispersed in AOT, the magnitude of the scattering vectors, q follows the ratio 1:√3:√4 corresponding to the (1,0), (1,1), and (2,0) reflections from a 2-D hexagonal lattice indicating the retention of the H2 phase. The d spacings for these systems were calculated and are presented in Table 3.2. The lattice parameters were calculated to be 24.55, 26.67, and 26.11 Å for the pure H2 phase, C6-GNP-dispersed H2 phase, and 10CB-GNP-dispersed H2 phase, respectively, which belong to the P6mm space group. This fact
along with the POM textures discussed previously supports our conclusion that this system exhibits a reverse hexagonal columnar phase (H2) even after the incorporation of the gold nanoparticles.

![Graph](image)

Figure 3.6: scattering vector vs. intensity plot obtained from the SAXS for a) pure AOT, b) C6-GNP/AOT and c) 10CB-GNP/AOT systems

Table 3.2: The $d$ values in Å for the AOT system and 1 mg of GNP/AOT dispersion measured by SAXS at room temperature

<table>
<thead>
<tr>
<th></th>
<th>$d_1$</th>
<th>$d_2$</th>
<th>$d_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure AOT</td>
<td>21.26</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C6-GNP/AOT</td>
<td>23.1</td>
<td>13.33</td>
<td>11.61</td>
</tr>
<tr>
<td>10CB-GNP/AOT</td>
<td>22.61</td>
<td>13.01</td>
<td>11.33</td>
</tr>
</tbody>
</table>

The pure AOT shows only one peak while the dispersions show additional peaks in the ratio of 1:$\sqrt{3}$:$\sqrt{4}$. This indicates that the dispersions of GNPs enhance the liquid crystalline order of the AOT system. The $d$ spacings of the dispersions have been observed to increase compared to the pure AOT system. The $d$ value obtained for the pure AOT system is 21.26 Å which is in good agreement with the reported value in the literature [31; 33]. The addition of GNPs increased the $d$ spacing for both the C6-GNP and the 10CB-GNP dispersions as seen in Table 3.2 and the maximum increase is observed in the C6-GNP dispersion where the $d$ spacing is 23.10 Å. For the C6-GNPs due to the presence of the hydrophobic terminal groups, they can be accommodated within the hydrophobic surface of the reverse
hexagonal phase of AOT, which results in the increase in \( d \) spacing. For the 10CB-GNPs, there was a small increment in the \( d \) values to 22.61 Å.

Since the increment in \( d \) values is small, we conclude that the GNPs are present outside the columns of the H2 phase. Moreover, for the H2 phase, the outer surface of the columns is hydrophobic and the inner core is hydrophilic. The thiol stabilised GNPs being hydrophobic, will prefer to occupy the outer hydrophobic surface of the hexagonal columns. For the 10CB-thiolated nanoparticles due to its polar cyano group, the outer surface of these GNPs is less hydrophobic as compared to the C6-GNPs. This results in a weaker interaction between the terminal groups of GNPs and the outer surface of the H2 phase and a very small increment in the \( d \) values.

From the above studies, we have concluded that the nanoparticles are present outside the cylindrical micellar columns irrespective of the H1 or H2 phase used as the liquid crystalline medium. In the H1 phase, the GNPs prefer to stay outside the columns due to the freely available space between the columns which provides a net entropic gain. In the H2 phase the outer surface of the hexagonal columns are hydrophobic and this additional factor also prefer the nanoparticles to be present in the hydrophobic region. It is observed that in both the phases, the addition of GNPs has enhanced the hexagonal order of the liquid crystalline phase with additional Bragg peaks. These results indicate that the Triton X-100/water system and the AOT system provide a very good medium for the dispersion of nanoparticles which can be used as model systems for different applications.

3.3 Ionic conductivity studies of the H1 phase

Though the H1 phase of Triton X-100/water system is quite well known and its phase behaviour is well studied, there is little information on the ionic conductivity. For example, the ionic conductivity of many of the surfactant systems has been studied in the literature except for the nonionic surfactants which contain polyethoxy chains. Triton X-100 molecules have the polyethoxy chains, the groups that form part of conducting membranes and possess significant ionic conductivity.

The polyethoxy membranes are also finding importance in the proton exchange fuel cell devices as their ionic conductivity is quite high compared to other membranes. Eventhough
the polyethoxy chains can not form any self-organised structures in the aqueous medium like liquid crystals, their proton conductivity is very high in presence of other ions. A survey in the literature shows that the proton conducting nature of these chains have not been explored much.

This section describes our experimental results of ionic conductivity studies in the H1 phase of Triton X-100/water system, which show surprisingly high ionic conductivity. The effect of dispersion of different dopants is also discussed in the present section. The high ionic conductivity can be explained on the basis of Grotthus mechanism, which is based on the extended water chain network model. A similar mechanism has also been proposed to explain the high ionic conductivity of protein dispersions in aqueous solutions [34; 35; 36; 37] and for water inside the carbon nanotubes [38].

3.3.1 Experimental Section

Triton X-100 was obtained from Aldrich and was used as received. All the solutions were prepared using millipore water having a resistivity of 18 MΩ.cm. Urea was obtained from Rankem. The lyotropic hexagonal columnar liquid crystalline phase (H1 phase) was prepared following the method as described in the previous section that contains 42 weight% of Triton X-100 and 58 weight% of water. The dispersions of gold nanoparticles and urea were prepared using the same procedure as described in the previous section. The concentration of GNPs were restricted at low levels as at high concentration, due to the steric interactions, the phase was observed to be unstable. The ionic conductivity of these samples were measured while cooling from the isotropic phase using a lock-in-amplifier (Stanford Research Systems, model SR830). Two platinum foil electrodes in the parallel plate configuration were used as the electrodes for the conductivity measurements. A schematic representation of the measurement setup is depicted in Figure 3.7. The current across the resistor R was measured and from which the ionic conductivity of the H1 phase was calculated.

3.3.2 Results and discussion

Figure 3.8 shows the ionic conductivity of the H1 phase formed by the Triton X-100/water system as a function of frequency that was measured at room temperature. It can be noted that
the conductivity has a plateau region in the 500 Hz to 10 kHz. At higher frequencies, the ionic conductivity decreases significantly due to the slow relaxation effects. At frequencies below 500 Hz, there is a small decrease in the ionic conductivity. Based on these observations, we have measured the conductivity of these systems at a frequency of 2 kHz.

Figure 3.9 shows the ionic conductivity of the HI phase as a function of temperature while cooling from the isotropic phase of the system. It is observed from the figure that the conductivity of the system is very high, of the order of several hundred μS/cm. This is contrary to the conductivity of pure water which is about 0.05 μS/cm. The phase transition from the HI phase to the isotropic phase can be clearly observed in the conductivity vs. temperature plot of Figure 3.9 which occurs at 32°C.

We have prepared aqueous solutions with different concentrations of Triton X-100, which is below the concentration corresponding to the formation of the liquid crystalline phase. The ionic conductivity of these samples are shown in Figure 3.10. It is observed that the ionic conductivity of these samples increases with the concentration of the surfactant. Since the pH of the solution is observed to be constant, the contribution from the dissolved CO₂ towards the conductivity can be ruled out. It also indicates the absence of any dissociation of the
surfactants to form ionic species in the system, which in any case is not reasonable within the experimental conditions since it is a nonionic surfactant. These observations point to a different kind of mechanism, *i.e.* Grotthus mechanism which operates in these systems.

### 3.3.2.1 Grotthus Mechanism

The high ionic conductivity of water was first explained by Grotthus in the year 1806 [39]. According to the Grotthus mechanism, the proton conductivity arises due to the presence of different hydrated protons in the system. Among several solvated protons, the most prominent clusters are the hydronium ion $\text{H}_3\text{O}^+$, the Zundel cation, $\text{H}_5\text{O}_2^+$ and the Eigen cation $\text{H}_9\text{O}_4^+$. The $\text{H}_3\text{O}^+$ is just a protonated water molecule with pyramidal structure. Under normal conditions, one water molecule can form hydrogen bonds with 4 different water molecules, two using the hydrogen atoms and two using the oxygen atom. On the other hand, the $\text{H}_3\text{O}^+$ ion can form maximum three hydrogen bonds with other water molecules, two using the hydrogen atoms and one using the oxygen atom. In the Zundel cation, the proton is shared between two water molecules, while in the Eigen cation, three water molecules are present in the first solvation layer of the hydronium ion. Due to the presence of three solvated water molecules, the Eigen cation is more stable compared to the Zundel cation [40; 41; 42].

Figure 3.8: Ionic conductivity of the H1 phase of Triton X-100/water system as a function of frequency at room temperature
Figure 3.9: Ionic conductivity of the H$_1$ phase of Triton X-100/water system as a function of temperature measured at different frequencies

The very high proton conductivity arises from the proton transport through these water clusters, viz, Zundel cations and Eigen cations. Eventhough different mechanisms have been proposed for the proton transfer pathways through these clusters, the most accepted mechanism is the E-Z-E pathway. Here, the proton transfer occurs from one oxygen atom to the other in an Eigen cation through the formation of an intermediate Zundel cation, as represented in Figure 3.11.

There are several speculations over the kinetics of the proton transfer mechanisms in these protonated water clusters. The rate limiting step in the proton transfer process may be either proton motion or the structural diffusion. Structural diffusion means the addition of water molecules to the solvation layer of the protonated clusters. Experimental results using deuterium showed that the isotropic effect is 1.4 instead of the expected value of 2 for the proton motion \cite{40}. This indicates that the proton motion is not the rate limiting step. Since every water molecule can form 4 hydrogen bonds at a time as described above, the validity of structural diffusion process as the rate determining step may be ruled out. The NMR studies on proton hopping process indicate that the hydrogen-bond cleavage is the rate limiting step \cite{43}. Moreover, the cleavage needs a reorientation of water molecules and under such a condition, the isotropic effect may be given by $\sqrt{m_D/m_H}$, where $m_D$ is the atomic weight of deuterium (2) and $m_H$ is atomic weight of hydrogen. This gives an isotropic effect value of $\sqrt{2}$ or 1.4, which is in agreement with the experimental results on the kinetics of the reaction.
Figure 3.10: Ionic conductivity of the Triton X-100/water system as a function of the concentration of Triton X-100 [40].

Figure 3.11: Schematic diagram of the proton transfer by Grotthus mechanism

In the liquid crystalline phase, due to the close packed arrangement of water molecules on the surface of the micelles, a well ordered network of hydrogen bonding water molecules is possible. This hydrogen bonding network provides a facile proton transfer pathway. Any release of free protons in the H1 phase is ruled out as the pH of the solution is constant irrespective of the concentration of the surfactant. The ionic conductivity shows a plateau at concentrations of Triton X-100 corresponding to the formation of columnar hexagonal phase as shown in Figure 3.10. This indicates the significant role of extended hydrogen-bond network in the ionic conductivity values. We have also observed that above this concentration, there is a very little increase in the conductivity with the increase in the concentration of the surfactant, which may be ascribed to the saturation of the hydrogen bonded network.
The lyotropic columnar hexagonal liquid crystalline phase that is used in the present studies is formed by cylindrical micelles of Triton X-100 surfactant molecules in the aqueous medium. The surfactants are self-organised into the cylindrical micelles which are surrounded by water molecules. These water molecules, due to the hydrophilic-hydrophilic interactions with the polyethoxy chains, are strongly attached to the micelles. This is similar to the water molecules which are attached to the protein molecules in the biological systems. This provides a route for the formation of clusters of protonated water molecules like hydronium, Zundel and Eigen cations. The existence of similar water clusters has been proposed in a variety of systems like water inside carbon nanotubes and on the protein surface. Since these protonated water clusters are in close vicinity to each other on the micellar surface, proton transfer between these clusters are facile and hence the ionic conductivity increases. It has been proposed in the literature that such water clusters facilitate the transport of protons through the water-chains by Grotthus mechanism [34; 35; 36; 37].

For verifying the role of these cationic clusters in the ionic conductivity, we have measured the ionic conductivity of the H1 phase at different concentrations of urea. Urea is a well known reagent for the denaturation of protein systems by the distruction of hydrogen bonding network [44; 45]. Such materials are commonly known as chaotropic reagents. Similar effect of disruption of hydrogen bonded water network formed in the PEO chains is expected in the addition of urea. Figure 3.12 shows the ionic conductivity as a function of temperature for the different concentrations of urea. It is observed that the conductivity decreases as the concentration of urea increases. This indicates that the addition of urea disrupts the hydrogen-bonded networks, which is responsible for the decrease in the ionic conductivity. At lower concentrations of urea there is a negligible decrease in the conductivity while above 5 M concentration, it decreases drastically. It has been shown that 8 M urea is sufficient to denature proteins in aqueous solutions [45]. Our results are in agreement with these reports.

We have also studied the effect of addition of gold nanoparticles in the ionic conductivity of the H1 phase. Figure 3.13 shows the ionic conductivity as a function of temperature for the H1 phase of Triton X-100/water system before and after GNP dispersion. It is clear from the figure that the ionic conductivity has increased after GNP dispersion. The hexanethiolated gold nanoparticles have hydrophobic terminal groups, which are present in between
Figure 3.12: Ionic conductivity of the H1 phase as a function of temperature for Triton X-100/water system dispersed with different concentrations of urea, \( \circ \) (0 M), \( \bullet \) (0.5 M), \( \square \) (1 M), \( \blacksquare \) (5 M), \( \triangle \) (8 M) and \( \blacktriangle \) (9 M)

the columns and domain spaces as described in the previous section. As a result of this, the water molecules are aggregated more strongly to the micellar surface, which improves the hydrogen-bonded network and the ionic conductivity. This is in agreement with the SAXS studies described in the previous section, where we have shown that the \( d \) spacing of the GNP dispersed H1 phase is decreased compared to the pure H1 phase, which indicates a stronger water aggregation on the cylindrical micellar surface formed by the Triton X-100 surfactant.

The H1 phase provides a simple model for studying the behaviour of water clusters in different systems like on the protein surfaces. As described in chapter 2, the redox probes like ferrocyanide/ferricyanide and hexaaammineruthenium molecules are less hydrated in the H1 phase as compared to the aqueous medium. These results are in agreement with the present model, as most of the water molecules are attached to the micellar surface, that leads to a higher ionic conductivity. As the concentration of the chaotropic agent increases, the hydrogen bonding network disrupts resulting in the lowering of proton conductivity, while addition of gold nanoparticles increases the hydrogen-bonded network and the ionic conductivity.
3.4 Conclusion

The dispersion of thiol-protected gold nanoparticles in two columnar hexagonal systems are studied. The results show that the addition of nanoparticles at lower concentrations have retained the liquid crystalline phase, with an enhancement in the order within the phase. The SAXS studies show that the nanoparticles occupy the inter-domain space rather than inside the core of the cylindrical micelles.

From the conductivity studies of the H1 phase of the pure Triton X-100/water system and the dispersions, it is proposed that the system contains the protonated water clusters which are responsible for the high ionic conductivity. Proton conductivity is a complex process and clearly there are several issues which have to be addressed in order to fully understand the phenomenon of ionic conductivity in the liquid crystalline phase formed by nonionic surfactants. For example, a detailed study is necessary for establishing the different hydronium ions present in the system. This simple system may be used as a model system for the study of the proton transfer reaction mechanism and the structure of water on the protein surfaces.
Bibliography


